FIP10601 – Text 11

Interacting electrons in the homogeneous limit

The e-e interaction term as it appears in the second-quantization version of the electronic Hamiltonian was derived in Text 10. It involves the matrix element

$$U_{\mathbf{k}_1'\mathbf{k}_2';\mathbf{k}_2\mathbf{k}_1} = \int \mathrm{d}^3r \int \mathrm{d}^3r' \, \psi_{\mathbf{k}_1'}^*(\mathbf{r})\psi_{\mathbf{k}_2'}^*(\mathbf{r}')U(\mathbf{r}-\mathbf{r}')\psi_{\mathbf{k}_2}(\mathbf{r}')\psi_{\mathbf{k}_1}(\mathbf{r}) \, . \tag{1}$$

Here, $\psi_{\mathbf{k}}(\mathbf{r})$ is a Bloch function, and therefore carries information about the lattice through the modulating function $u_{\mathbf{k}}(\mathbf{r})$ when written as

$$\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})\mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} \, . \tag{2}$$

If the system has a reasonably homogeneous electron density, we can simplify the calculation of this kind of matrix element using a homogeneous approximation in which $u_{\mathbf{k}}(\mathbf{r})$ is reduced to the normalization constant $1/\sqrt{V}$. We will restrict ourselves to this case, which is appropriate to discuss interaction effects in weakly-correlated (wide-band) systems. We then have

$$\begin{aligned}
U_{\mathbf{k}_1'\mathbf{k}_2';\mathbf{k}_2\mathbf{k}_1} &= \frac{1}{V^2} \int \mathrm{d}^3r \int \mathrm{d}^3r' \, \mathrm{e}^{-\mathrm{i}(\mathbf{k}_1'-\mathbf{k}_1)\cdot\mathbf{r}} \, \mathrm{e}^{-\mathrm{i}(\mathbf{k}_2'-\mathbf{k}_2)\cdot\mathbf{r}'} \, U(\mathbf{r}-\mathbf{r}') \\
&= \frac{1}{V} \int \mathrm{d}^3r' \, \mathrm{e}^{-\mathrm{i}(\mathbf{k}_2'-\mathbf{k}_2+\mathbf{k}_1'-\mathbf{k}_1)\cdot\mathbf{r}'} \frac{1}{V} \int \mathrm{d}^3r \, \mathrm{e}^{-\mathrm{i}(\mathbf{k}_1'-\mathbf{k}_1)\cdot(\mathbf{r}-\mathbf{r}')} \, U(\mathbf{r}-\mathbf{r}') \, .
\end{aligned} \tag{3}$$

Even though we are evaluating integrals in a finite volume V, periodic boundary conditions imply that the integration on $\mathbf{r}$ is independent of $\mathbf{r}'$. Then the integration on $\mathbf{r}'$ can be performed, and we have

$$\frac{1}{V} \int \mathrm{d}^3r' \, \mathrm{e}^{-\mathrm{i}(\mathbf{k}_2'-\mathbf{k}_2+\mathbf{k}_1'-\mathbf{k}_1)\cdot\mathbf{r}'} = \delta_{\mathbf{k}_2'-\mathbf{k}_2,\mathbf{k}_1-\mathbf{k}_1'} \, , \tag{4}$$

indicating *"momentum" conservation* in the interaction process.

Defining the *transferred wavevector* $\mathbf{q} \equiv \mathbf{k}_1' - \mathbf{k}_1 = \mathbf{k}_2 - \mathbf{k}_2'$, we obtain

$$U_{\mathbf{k}_1'\mathbf{k}_2';\mathbf{k}_2\mathbf{k}_1} = U(\mathbf{q}) \, \delta_{\mathbf{k}_1',\mathbf{k}_1+\mathbf{q}}\delta_{\mathbf{k}_2',\mathbf{k}_2-\mathbf{q}} \, , \tag{5}$$

where $U(\mathbf{q})$ is the Fourier transform of the interaction potential,

$$U(\mathbf{q}) = \frac{1}{V} \int \mathrm{d}^3r \, \mathrm{e}^{-\mathrm{i}\mathbf{q}\cdot\mathbf{r}} \, U(\mathbf{r}) \, . \tag{6}$$

Finally, with a further change of summation variables ($\mathbf{k}_1 \to \mathbf{k}$ and $\mathbf{k}_2 \to \mathbf{k}'$), the Hamiltonian can be written as

$$\mathcal{H} = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} \, c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma} + \frac{1}{2} \sum_{\substack{\mathbf{k}\mathbf{k}'\mathbf{q} \\ \sigma\sigma'}} U(\mathbf{q}) \, c_{\mathbf{k}+\mathbf{q},\sigma}^\dagger c_{\mathbf{k}'-\mathbf{q},\sigma'}^\dagger \, c_{\mathbf{k}'\sigma'} \, c_{\mathbf{k}\sigma} \, . \tag{7}$$

Using the explicit form of the Coulomb potential,

$$U(\mathbf{r}) = \frac{\kappa\, e^2}{r} \,, \tag{8}$$

we have

$$U(\mathbf{q}) = \frac{\kappa\, e^2}{V} \int \mathrm{d}^3 r \, \frac{\mathrm{e}^{-i\mathbf{q}\cdot\mathbf{r}}}{r} \,. \tag{9}$$

At least for the case $\mathbf{q} = 0$, the above integral diverges in the limit $V \to \infty$. On the other hand, the factor $1/V$ tends to zero in this same limit, but it should be borne in mind that the interaction term in the Hamiltonian contains a sum over all pairs of particles, which also involves a volume factor (for fixed density). Therefore, we need to examine carefully the possibility of divergence of the energy per particle.

Regularization of the interaction potential

To preserve the spirit of treating a finite-volume system with periodic boundary conditions, we need an interaction range that does not exceed the system size. So, let us replace $U(\mathbf{r})$ by

$$U_\alpha(\mathbf{r}) \equiv \lim_{\alpha\to 0} \frac{\kappa\, e^2}{r}\mathrm{e}^{-\alpha r} \,, \tag{10}$$

with α sufficiently large to ensure that the interaction drops to zero within the volume V. When $V \to \infty$, one can take $\alpha \to 0$, recovering Eq. (8). Thus, for consistency the thermodynamic limit must be taken **before** the limit $\alpha \to 0$.

The Fourier transform can be easily evaluated using spherical coordinates. We can extend the integration in r to infinity, since the exponential in the integrand becomes negligible before r reaches the system limits. The result is

$$U_\alpha(\mathbf{q}) = \frac{4\pi}{V} \frac{\kappa\, e^2}{q^2 + \alpha^2} \,. \tag{11}$$

It is still not clear what happens after the double limit $V \to \infty$, $\alpha \to 0$. However, it is clear that there is no problem for $q \neq 0$. Let us then separately evaluate the $\mathbf{q} = 0$ term in the interaction Hamiltonian,

$$U_0 = \frac{2\pi\kappa\, e^2}{V\alpha^2} \sum_{\substack{\mathbf{k}\mathbf{k}' \\ \sigma\sigma'}} c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}'\sigma'}^\dagger c_{\mathbf{k}'\sigma'} c_{\mathbf{k}\sigma} \,. \tag{12}$$

Using the algebra of fermion operators, we can write

$$
\begin{aligned}
c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}'\sigma'}^\dagger c_{\mathbf{k}'\sigma'} c_{\mathbf{k}\sigma} &= -c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}'\sigma'}^\dagger c_{\mathbf{k}\sigma} c_{\mathbf{k}'\sigma'} \\
&= -c_{\mathbf{k}\sigma}^\dagger (\delta_{\mathbf{k}\mathbf{k}'}\delta_{\sigma\sigma'} - c_{\mathbf{k}\sigma} c_{\mathbf{k}'\sigma'}^\dagger) c_{\mathbf{k}'\sigma'} \,.
\end{aligned}
\tag{13}
$$

Therefore,

$$
\begin{aligned}
U_0 &= \frac{2\pi\kappa\,e^2}{V\alpha^2}\left[\sum_{\mathbf{k}\sigma}c^\dagger_{\mathbf{k}\sigma}c_{\mathbf{k}\sigma}\sum_{\mathbf{k}'\sigma'}c^\dagger_{\mathbf{k}'\sigma'}c_{\mathbf{k}'\sigma'}-\sum_{\mathbf{k}\sigma}c^\dagger_{\mathbf{k}\sigma}c_{\mathbf{k}\sigma}\right]\\
&= \frac{2\pi\kappa\,e^2}{V\alpha^2}\left[\sum_{\mathbf{k}\sigma}\hat{n}_{\mathbf{k}\sigma}\sum_{\mathbf{k}'\sigma'}\hat{n}_{\mathbf{k}'\sigma'}-\sum_{\mathbf{k}\sigma}\hat{n}_{\mathbf{k}\sigma}\right]\\
&= \frac{2\pi\kappa\,e^2}{V\alpha^2}(N^2-N)\;,
\end{aligned}
\tag{14}
$$

where the last equality enforces the restriction to a subspace of fixed number of particles.

In the thermodynamic limit, we must focus on the energy **per particle**. Using the particle density $n = N/V$ (which is finite), we have

$$
\frac{U_0}{N}=\frac{2\pi\kappa\,e^2 n}{\alpha^2}\left(1-\frac{1}{N}\right)\xrightarrow[N\to\infty]{}\frac{2\pi\kappa\,e^2 n}{\alpha^2}\;.
\tag{15}
$$

So, having carefully taken the thermodynamic limit, we see that U_0/N **diverges** for $\alpha \to 0$. This divergence indicates an instability due to the fact that we have considered only the repulsive interaction between electrons. We must also consider the presence of the ions, which guarantee *charge neutrality*. In the **homogeneous limit**, the ions are replaced by a uniform distribution of positive charges (*jellium model*). The self-interaction energy of such a charge distribution, as well as its interaction with the electrons can be easily evaluated (**EXERCISE**). The same α must be used to regularize the Coulomb potential in all cases. This procedure shows that

- the self-interaction of positive charges gives a repulsive term **equal** to the one obtained for electrons;
- the interaction between positive charges and electrons gives an attractive term that exactly **compensates** the other two.

In summary, the $\mathbf{q} = 0$ term is suppressed from the interaction Hamiltonian when charge neutrality is taken into account. That done, we can drop the regularization parameter α. This corresponds to writing the electronic Hamiltonian with

$$
U(\mathbf{q})=\frac{4\pi}{V}\frac{\kappa\,e^2}{q^2}\left(1-\delta_{\mathbf{q}0}\right)\;,
\tag{16}
$$

which will be the form adopted hereafter. Note that, although the divergence strictly at $\mathbf{q} = 0$ has been eliminated, the dominant region still corresponds to small values of q. This is important to the simplifying assumptions employed here, since a large wavevector transfer would introduce a reciprocal-lattice vector in the conservation condition of Eq. (5), implying non-trivial modulation functions $u_{\mathbf{k}}(\mathbf{r})$. The dominance of small $\mathbf{q}$ indicates that such changes would only be important for Fermi surfaces very close to Brillouin-zone boundaries.

Parametrization of the Hamiltonian

In order to analyze the relative importance of kinetic energy and Coulomb interaction, we will explicitly extract the energy and length scales of the problem, rewriting the Hamiltonian in terms of these scale factors and dimensionless variables. For this, we first define a length r_0 (known as *Wigner radius*) as the radius of an *effective* spherical volume occupied by each electron. Thus,

$$\frac{4}{3}\pi r_0^3 = \frac{V}{N} \quad \Rightarrow \quad r_0 = \left(\frac{3}{4\pi n}\right)^{1/3} . \tag{17}$$

Next we introduce a dimensionless parameter r_s, defined as

$$r_s \equiv \frac{r_0}{a_0} , \qquad a_0 = \frac{\hbar^2}{m\kappa\, e^2}. \tag{18}$$

So, the Bohr radius a_0 is the length scale, and the electron density is parametrized by r_s, being proportional to r_s^{-3}. We can now define a *dimensionless wavevector*

$$\bar{\mathbf{k}} \equiv r_0 \mathbf{k} = r_s\, a_0 \mathbf{k} . \tag{19}$$

In order to extract the energy scale, let us consider a parabolic band (which is compatible with the homogeneous limit) with effective mass m^*. Then,

$$\varepsilon_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m^*} = \left(\frac{m}{m^*}\right)\frac{1}{2}\kappa\, e^2 a_0 k^2 = \left(\frac{\kappa\, e^2}{2a_0}\right)\left(\frac{m}{m^*}\right)\frac{\bar{k}^2}{r_s^2} . \tag{20}$$

This reveals the energy scale as being $(\kappa\, e^2/2a_0)$, which is $1\,\mathrm{Ry} \simeq 13.6$ eV.

Writing the potential $U(\mathbf{q})$ also in terms of dimensionless quantities, we have

$$U(\mathbf{q}) = \frac{4\pi\kappa\, e^2}{V q^2} = \frac{3\kappa\, e^2}{r_0^3 N q^2} = \frac{6}{N}\left(\frac{\kappa\, e^2}{2a_0}\right)\frac{1}{r_s \bar{q}^2} . \tag{21}$$

The Hamiltonian can then be written as

$$\mathcal{H} = \left(\frac{\kappa\, e^2}{2a_0}\right)\frac{1}{r_s^2}\left[\left(\frac{m}{m^*}\right)\sum_{\mathbf{k}\sigma}\bar{k}^2 c_{\mathbf{k}\sigma}^{\dagger}c_{\mathbf{k}\sigma} + 3\, r_s\frac{1}{N}\sum_{\substack{\mathbf{k}\mathbf{k}'\mathbf{q}\\ \sigma\sigma'}}\frac{1}{\bar{q}^2}\, c_{\mathbf{k}+\mathbf{q},\sigma}^{\dagger}c_{\mathbf{k}'-\mathbf{q},\sigma'}^{\dagger}\, c_{\mathbf{k}'\sigma'}\, c_{\mathbf{k}\sigma}\right] . \tag{22}$$

Taking into account that the factor $1/\bar{q}^2$ in the interaction term makes the sum over $\mathbf{q}$ finite, the factor $1/N$ can be associated to one of the wavevector sums to yield a finite result in the thermodynamic limit.

To judge the relative importance of kinetic and interaction energies, we must note that the latter has an extra factor r_s. Therefore, the e-e interaction term could be treated **perturbatively** if $r_s \ll 1$. However, this **does not** happen. From the observed densities of real metals it follows that $r_s \sim 2 - 6$.

It is interesting to observe that, in a somewhat non-intuitive way, the interaction between electrons becomes **less** important as the electron **density increases**. This can be understood as a quantum enhancement of kinetic energy due to higher confinement (lower effective volume per electron). The kinetic energy increases proportionally to r_s^{-2}, while the potential energy also increases, but in proportion to r_s^{-1}, so that its **relative** importance is reduced as r_s decreases.

Hartree-Fock approximation revisited

Let us go back to the evaluation of the ground-state energy, addressed in Text 9, but now using the second-quantization electronic Hamiltonian. It follows from Eq. (7) that

$$E_0 = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} \langle \hat{n}_{\mathbf{k}\sigma} \rangle + \frac{1}{2} \sum_{\substack{\mathbf{k}\mathbf{k}'\mathbf{q} \\ \sigma\sigma'}} U(\mathbf{q}) \, \langle c_{\mathbf{k}+\mathbf{q},\sigma}^{\dagger} c_{\mathbf{k}'-\mathbf{q},\sigma'}^{\dagger} c_{\mathbf{k}'\sigma'} c_{\mathbf{k}\sigma} \rangle \,, \tag{23}$$

where the averages refer to the ground state. The Hartree-Fock approximation implies an independent-electron ground-state. This is nothing but the *Fermi sea*, corresponding to $N/2$ single-particle $\mathbf{k}$-states of increasing wavevector magnitude up to a limiting value k_F, each appearing twice due to the two spin states.

The single-particle term in Eq. (23) is trivial. Let us analyze the average appearing in the interaction-term. The two annihilation operators suppress two electrons from occupied states, leaving **holes** in $\mathbf{k}\sigma$ and $\mathbf{k}'\sigma'$. The two creation operators should then create two electrons, **recovering** the initial ground-state. Therefore, there are only two possibilities:

1) $\mathbf{k} + \mathbf{q} = \mathbf{k}$, $\mathbf{k}' - \mathbf{q} = \mathbf{k}'$ (keeping the initial spins);

2) $\mathbf{k} + \mathbf{q} = \mathbf{k}'$, $\mathbf{k}' - \mathbf{q} = \mathbf{k}$ $\Rightarrow \sigma' = \sigma$.

The first possibility is the Hartree term. It implies $\mathbf{q} = 0$, thus being eliminated by the condition $U(0) = 0$ in the homogeneous case considered here. The second possibility is the exchange contribution, which can be rearranged as

$$
\begin{aligned}
\langle c_{\mathbf{k}'\sigma}^{\dagger} c_{\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}'\sigma} c_{\mathbf{k}\sigma} \rangle &= -\langle c_{\mathbf{k}'\sigma}^{\dagger} c_{\mathbf{k}'\sigma} c_{\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}\sigma} \rangle \\
&= -\langle \hat{n}_{\mathbf{k}'\sigma} \hat{n}_{\mathbf{k}\sigma} \rangle \\
&= -\langle \hat{n}_{\mathbf{k}'\sigma} \rangle \langle \hat{n}_{\mathbf{k}\sigma} \rangle \,,
\end{aligned}
\tag{24}
$$

where the last decomposition of the average is due to particle independence in the Hartree-Fock ground-state.

From this analysis, the ground-state energy in the Hartree-Fock approximation is

$$E_0^{\mathrm{HF}} = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} \langle \hat{n}_{\mathbf{k}\sigma} \rangle - \frac{1}{2} \sum_{\mathbf{k}\mathbf{k}'\sigma} U(\mathbf{k}' - \mathbf{k}) \, \langle \hat{n}_{\mathbf{k}'\sigma} \rangle \langle \hat{n}_{\mathbf{k}\sigma} \rangle \,. \tag{25}$$

Given the nature of the ground state, we have

$$\langle n_{\mathbf{k}\sigma} \rangle = \theta(k_F - k) \,, \tag{26}$$

where $\theta(x)$ is the Heaviside function. Then, using the parametrization with r_s, as in Eq. (22), and turning the sums over $\mathbf{k}$ into integrals, we can explicitly evaluate the ground-state energy (**EXERCISE**), which can be written as

$$\frac{E_0^{\mathrm{HF}}}{N} = \left(\frac{\kappa\, e^2}{2a_0} \right) \left[\left(\frac{m}{m^*} \right) \frac{2.21}{r_s^2} - \frac{0.916}{r_s} \right] \,. \tag{27}$$

It is interesting to make a contact with DFT, whose main feature is to express the ground-state energy as a functional of the electronic density. Here, E_0^{HF} is a **function** of r_s, which parametrizes a uniform density. Thus, to determine the ground-sate density we simply minimize E_0^{HF} with respect to r_s. The result is $r_s = 4.83\,(m/m^*)$. This value becomes "universal" for $m^* = m$, since this corresponds to suppressing the external-potential term in Eq. (29) of Text 9, reducing $E[\rho]$ to the functional $F[\rho]$. Besides, since the Hartree term is null, $F[\rho]$, written as in Eq. (36) of Text 9, contains only $T_0[\rho]$, and $E_{\mathrm{xc}}[\rho]$, respectively given by the two terms on the right-hand side of Eq. (27), without mass correction in the first. The E_{xc} part is actually due to exchange only, since the Hartree-Fock approximation does not take correlations into account.

It is worth mentioning that the value $r_s = 4.83$, obtained in the strictly homogeneous limit, lies within the experimental range previously mentioned, being particularly close to the value 4.86 observed for potassium.[1] This could be viewed as a relative success of the Hartree-Fock approximation, despite its intrinsic limitations.

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[1]All the noninteger numbers quoted in this page are approximations to three significant digits.